

PATENT SPECIFICATION

999,857



NO DRAWINGS.

999,857

Inventors: PERCY ROY CLEMOW, RALPH
GORDON HARRY, KENNETH JOHN FRANKLIN.

Date of filing Complete Specification: July 8, 1963.
Application Date: July 17, 1962.
Complete Specification Published: July 28, 1965.
© Crown Copyright 1965.

No. 27448/62.

Index at acceptance:—A5 B32

Int. Cl.:—A 61 k 7 / 16

COMPLETE SPECIFICATION

Toothpastes

We, INTERNATIONAL CHEMICAL COMPANY LIMITED, of 12 Chenies Street, London, W.C.1, a British Company, do hereby declare the invention for which we pray that a patent 5 may be granted to us and the method by which it is to be performed, to be particularly described in and by the following statement:

This invention relates to toothpastes and to processes for preparing them.

10 The therapeutic effect of fluoride in dentifrices is now well recognised and much research has been carried out on the formulation of fluorides in toothpastes. It has been known for some time that the cheaper abrasives, for example calcium carbonate, normally used in toothpastes inactivate fluorides by reducing the ionisable fluorine content of pastes containing them to such an extent that the fluoride exerts little beneficial therapeutic effect. As a result 15 research has been directed to the discovery of abrasives which less seriously inactivate fluorides, and this has led to the use of special types of abrasive which are more expensive. Moreover, past research has also led to the 20 general acceptance of the view that for a fluoride to retain its activity in a paste, the pH of the paste must be on the acid side of neutrality, thus making it impossible to use alkaline abrasives.

25 It has now been discovered that the inactivation of alkali metal fluoride in a toothpaste by calcium carbonate or other calcium or magnesium salt abrasives having a low water solubility can be substantially reduced by incorporating in the toothpaste silica in water-soluble form, so that it is possible for the first 30 time to formulate such a toothpaste retaining a satisfactory amount of ionisable fluorine, and thus to formulate an effective fluoride toothpaste containing an alkaline abrasive.

35 By silica in water-soluble form is meant a silicic acid or an alkali metal salt of silicic acid which is soluble in water to give either a true solution or a colloidal solution.

40 A toothpaste of the invention is one com-

prising a calcium or magnesium salt abrasive having a water-solubility of less than 0.01 g./100 cc. at 20°C., a therapeutic amount of an alkali metal fluoride and sufficient silica in water-soluble form (as defined above) to reduce the inactivation of the fluoride by the abrasive. 50

As alkali metal fluoride it is preferable to use sodium fluoride, but potassium or lithium fluoride can also be employed. Preferably the toothpaste is one prepared by incorporation of from 0.01 to 0.4%, especially 0.05 to 0.15%, by weight of ionisable fluorine as alkali metal fluoride. 55

The silica can be incorporated in the form of a silica sol, preferably of alkaline pH, as a water-dispersible aerogel, or as an aqueous solution of a sodium or other alkali metal silicate, for instance sodium silicate having a sodium oxide to silica ratio by weight of from 1 : 3.1 to 1 : 3.4. Conveniently an aqueous solution of sodium silicate of the type known as waterglass is used. Preferably the toothpaste is one prepared by incorporation of from 0.03 to 1.5% or as much as 3%, especially 0.15 to 0.6% by weight of silica in water-soluble form. 60

The abrasive preferably comprises calcium carbonate, and it is convenient to have the abrasive consisting substantially wholly of calcium carbonate. However, other abrasives of low water-solubility, for example tricalcium orthophosphate and calcium pyrophosphate, can be employed as minor or major ingredients of the abrasive, for instance in an abrasive containing a major proportion of calcium carbonate. Calcium carbonate has a solubility of about 0.0015 g./100 cc. at 20°C. and various figures up to 0.003 g./100 cc. have been reported for the solubility of tricalcium orthophosphate. The presence of significant amounts of a more water-soluble calcium abrasive, for example dicalcium orthophosphate, is to be avoided. Preferably a toothpaste contains from 20 to 60% by weight of abrasive. 65

70

75

80

85

90

[Pri.]

5 The pH of a toothpaste of the invention is on the alkaline side of neutrality, and usually from 9 to 10.8, more often from 10.0 to 10.6. The pH of a toothpaste can be adjusted after mixing by the addition of alkali if desired. By pH of the paste is meant the pH as measured on the mixture obtained by dispersing the paste with 4 times its weight of water.

10 A toothpaste of the invention may also contain such other of the normal ingredients of dentifrices as are compatible with fluorides, including humectants (for example, glycerol and sorbitol) detergents (for example, water-soluble alkali metal fatty acid salts, alkali metal

15 higher alkyl sulphates and sulphonates, and alkali metal salts of sulphonated monoglycerides of higher fatty acids), thickeners (for example, methyl cellulose, sodium carboxymethyl cellulose, and gum tragacanth),

20 flavouring agents (for example saccharin,

sodium cyclamate, oil of peppermint, oil of spearmint, and oil of anise), and preservatives. Usually from 0.5 to 5% of detergent, and from 0.5 to 5% of thickener by weight of the paste are employed.

25 The invention also provides a toothpaste comprising calcium carbonate as abrasive, an alkali metal fluoride and a water-soluble silicate, the ionisable fluorine content of the paste being from 0.025 to 0.1% by weight.

30 The invention also comprises a process of preparing a toothpaste in which the separate ingredients as described above are formulated by mixing them together.

35 The following test illustrates the effect of sodium silicate in reducing the inactivation of fluoride by calcium carbonate. Compositions A and B were prepared from the following materials by mixing them together in the relative amounts stated.

	A	B
Sodium fluoride	0.22	0.22
Water	31.1	31.1
Calcium carbonate	50.0	50.0
40% Aqueous sodium silicate (having an Na ₂ O: SiO ₂ ratio of about 1: 3.2)	1.0	—

45 The resulting pastes were analysed for their ionisable fluorine content immediately after mixing. Analysis was carried out by dilution with an amount of water twice the weight of the paste sample, mixing, centrifugation and determination of fluoride in the supernatant liquid. Samples of the pastes were stored in

closed containers for 2½ months at room temperature, and for 4 weeks at 40°C., respectively, and their ionisable fluorine content again determined. The results were as follows, the ionisable fluorine found being given as the proportion % of the amount incorporated in the paste.

Composition	A	B
Initial soluble fluoride	60%	25%
After 2½ months	44%	10%
After 4 weeks at 40°C	56%	7%

55 This shows clearly the efficacy of the silicate in reducing the insolubilisation of the fluoride.

The invention is illustrated by the following Example.

Sodium fluoride	0.22
40% Aqueous sodium silicate (having an Na ₂ O: SiO ₂ ratio of about 1: 3.2)	1.00
Calcium carbonate	52.22
Glycerol	20.00
Carboxymethylcellulose (sodium salt)	1.00
Sodium lauryl sulphate	1.13
Flavour and preservative	1.17
Water	23.26
	100.00

EXAMPLE

60 A toothpaste of the invention was prepared by mixing together the following ingredients (in finely-divided form where solid) in the proportions by weight given.

The pH of this paste as measured on the mixture obtained by dispersing the paste in 4 times its weight of water was 10.3.

5 Another paste similar in every way except that the aqueous sodium silicate was left out was also prepared. Samples of the resulting

pastes were analysed for their ionisable fluorine content (a) immediately after mixing, (b) after standing for 6 months at room temperature, and (c) after standing for 3 months at 10 40°C., with the following results.

Ionisable fluorine remaining

	(a)	(b)	(c)
Paste of the invention	46%	36%	29%
Paste without silicate	36%	25%	18.5%

These results show that the silicate exerts a substantial effect in preserving soluble fluoride in the fully formulated toothpaste.

15 In further tests, the stability of the paste of the invention was compared with three well-known commercial stannous fluoride tooth-

pastes, which will be designated respectively pastes A, B and C, by measuring the amount of soluble fluoride present in these pastes at 20 various periods after storage at a constant temperature of 40°C.

Soluble fluoride in parts per million

Paste of invention	Paste A	Paste B	Paste C
Initially	350	410	380
After 3 months	300	240	270
After 7 months	310	180	110
After 1 year	300	150	210

25 Evidence of the protection conferred by use of the toothpaste of the invention was obtained by measuring the increase of resistance of powdered dental enamel to acid attack using a method essentially the same as that described by Gershon, Neiditch and Lee, Drug and Cosmetic Industry, February 1958, at pages 251-3, 30 except that saliva was used instead of water for preparing a dilution of the toothpaste, and

for the blank titration. Comparison was made with fresh samples of two typical well-known commercial toothpastes containing stannous fluoride (pastes A and B), and the following results were obtained. The pH measured is that of the saliva with or without paste dispersed in it, using saliva 3 times the weight of paste.

Material tested	pH	Calcium dissolved (Milligrams)	% Reduction in calcium dissolved
Saliva	6.9	8.48	
„	6.7	8.45	
„	—	8.51	
Paste of this invention	9.0	6.37	24.9
„	9.1	6.44	24.0
„	9.1	6.60	22.2
Stannous fluoride paste A	5.9	6.28	25.9
„	—	6.52	23.1
Stannous fluoride paste B	6.0	6.67	21.3
„	—	6.67	21.3

These results demonstrate that the toothpaste of the invention, though based on calcium carbonate and sodium fluoride, was about as effective as the commercial toothpastes based on stannous fluoride and relatively expensive abrasives.

WHAT WE CLAIM IS:

1. A toothpaste comprising a calcium or magnesium salt abrasive having a water-solubility of less than 0.01 g./100 cc. at 20°C., a therapeutic amount of an alkali metal fluoride and sufficient silica in water-soluble form as herein defined to reduce the inactivation of the fluoride by the abrasive.
2. A paste according to Claim 1, in which the alkali metal fluoride is sodium fluoride.
3. A paste according to any preceding claim, in which the silica is incorporated in the form of an aqueous solution of an alkali metal silicate.
4. A paste according to Claim 3, in which the alkali metal silicate is a sodium silicate.
5. A paste according to any preceding claim, in which the abrasive comprises calcium carbonate.
6. A paste according to Claim 5, in which the abrasive is substantially wholly calcium carbonate.
7. A paste according to any preceding claim, in which is incorporated from 0.01 to 0.4%

35

8. A paste according to Claim 7, in which is incorporated from 0.05 to 0.15% by weight of ionisable fluorine as alkali metal fluoride.
9. A paste according to any one of Claims 1 to 8, in which is incorporated from 0.03 to 1.5% by weight of silica in water-soluble form.
10. A paste according to any one of Claims 1 to 8, in which is incorporated from 0.15 to 0.6% by weight of silica in water-soluble form.
11. A paste according to any preceding claim and having a pH of from 9 to 10.8.
12. A toothpaste comprising calcium carbonate as abrasive, an alkali metal fluoride and a water-soluble silicate, the ionisable fluorine content of the paste being from 0.025 to 0.1% of the weight of the paste.
13. A toothpaste containing silica substantially as described in the Example.
14. A process for preparing a toothpaste according to any preceding claim in which the ingredients of the paste are formulated by mixing them together.

40

45

50

55

60

65

70

75

80

85

90

95

G. H. HARGREAVES,
Chartered Patent Agent,
John Wyeth & Brother Limited,
Huntercombe Lane South,
Taplow, Maidenhead,
Berkshire.